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POLYMER SEMICONDUCTORS

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POLYMER SEMICONDUCTORS

[Following is the translation of an article by V. Azernikov in Nauka i Zhizn, (Science and Life), No 2, Moscow, 1961, pages 8-10.]

It seemed that polymers had already given us everything possible. They revealed their marvelous properties which made them a synonym of their very name: when we hear the word "polymer", our memory automatically throws the following epithets from the storehouse of recollection: elasticity, strength, electrical insulation, thermal stability. It is difficult to write about polymers. Surely all images, comparisons and hyperboles have been expended which would be used in an attempt to explain the unknown. It seemed that not so much the publicizers as the polymers themselves were at fault in this.

But nature is more generous than we think and often presents us with surprises, changing not only our opinion of the potentials but even the name of a particular era. In a comparatively short period of time the stormy 20th Century has acquired a good dozen names: the century of electricity, of radio, and of electronics, the atomic century, the century of semiconductors, of cybernetics, and of sputniks, the polymer century, etc. These discoveries did not always come to us as gifts causing joy by their very unexpectedness; most often they were the results of expensive and time-consuming searches.

One of the discoveries on the thorny road of science, reversing our conventional concepts of the supposed infallibility of inorganic substances, was the revelation of the fact that organic substances possess properties of semiconductors. As usual, scientists came across this phenomenon much earlier than they became interested in it. A half century ago it was noted that the hydrocarbon anthracene possessed photoconducting properties. But at the time no-one paid any attention to this. Time and progress in science as a whole were required for the chance to be announced as conforming to natural laws.

Between Two Extremes

Our earth is wrapped up in a web of steel wire. It stretches from pole to pole, plunges into the vents of substations, crawls into our homes as white serpents, bringing heat and light. The wires are of metal and the metal is a conductor. On the walls the wires are supported by white cleats. The cleats are of porcelain, and porcelain is an insulator. These self-evident truths were imbibed by us together with the milk of our school lessons. For a long time it seemed entirely convincing that substances are divided into two opposite classes: conductors and dielectrics, one or the other. Subsequently it became clear that things are not that simple. Certain substances fit neither in the one nor the other category, or more accurately, fitted both. More than that, these substances -- semi-conductors -- cross our paths more often than the classic antipodes. Academician A. F. Ioffe stated that semi-conductors made up almost the entire inorganic world surrounding us.

They are victorious not only in numbers but in abilities. Semi-conductors carried through a technical revolution due to their unlimited potential. They are able to transform alternating current into direct, thermal energy directly into electrical, they generate radio waves and amplify high frequency vibrations. This is not all. A simple enumeration of the potentials of semi-conductors would take up an entire chapter.

This universality and often simply indispensability of semi-conductors naturally caused heightened interest in the very phenomenon of semi-conductivity. For a long time it was connected exclusively with the crystalline structure of the solid body. However, comparatively recently Leningrad professor A. R. Regel' discovered these properties in solid substances in a fused state, where it was impossible to suspect crystallinity. But nevertheless these were inorganic substances. Now the last ramparts of old beliefs have fallen -- organic semi-conductors have appeared on the scene. The electrical conductivity of metals is connected with the presence of free valence electrons in them. This is a well-known fact. In crystalline semi-conductors the carriers of energy are electrons or "holes". This is also a known fact. What about organic molecules? Who conducts the energy in them?

Wandering Electrons

The basic feature distinguishing organic semi-con-

ductors is the presence of double bonds in their molecules. The bond can be single as in saturated combinations or double as in non-saturated. If single and double bonds alternate in a molecule, this is a conjugated system. In each group $-HC=CH-$, this unique "Conjugation brick", there are two so-called π -electrons. They are distinguished from their other brothers by a more freedom-loving "nature": they do not sit, bound to one spot, but are free to move along the molecule. Naturally only in case the conjugation chain is endless do double and single bonds alternate in strict sequence. The appearance in the molecular chain of any group which violates the conjugation breaks the interaction of π -electrons. This is the same as placing a piece of insulator into an electric wire.

Since the π -electrons wander along the conjugation chain, one may consider that they do not belong to one atom but to all of them. They are therefore called generalized electrons or delocalized. The delocalization of electrons is the reason for the "metal similarity" of organic molecules, their particular electrophysical properties. Electrical conductivity in a chain of conjugation is connected to a great degree with its geometry. The simpler the configuration of the molecule, the less it has of various breaks and branchings, and the greater is its electrical conductivity. In addition, the longer a chain is the more delocalized π -electrons it has, and the better its conductivity is. In order for electrons to become free, it is necessary for them to make the transition from a lower energy level to a higher. If these levels are far from each other, the electron of itself cannot surmount the "chasm" -- the energy barrier. Expenditures of energy are necessary, the energy of activation. The closer the levels, the less amount of activation energy and the better conductivity. When the conjugation chain is short, when there are few π -electrons, the levels are far apart. The interaction of a large number of electrons washes away clear-cut levels, and they crawl away in all directions, becoming broad strips. The more electrons interacting, naturally the wider the strips will be and the distance between the edges will be smaller; the energy "chasm" becomes smaller and conductivity increases. This is an extremely important condition. It engenders a definite program of action: it is necessary to "build" a molecule with an enormous conjugation chain for the creation of organic semi-conductors capable of competing with crystalline ones.

From Molecule to Polymer

Imagine that you were required to build a toothed, brick wall. How is this to be done? It is self-evident that it can be built from the ground up of brick, and it is also possible to take a completed wall and remove a few bricks equidistant from one another -- the teeth are achieved also in this manner. Although this analogy is not very close to the task faced by the chemists, at any rate the choice was the same. Macromolecules with total conjugation -- with polyconjugation -- can be synthesized, and it is possible to take a suitable molecule and "build" in it conjugated double bonds. How is this to be done?

The chemists were at a fork in the scientific road. If they went to the left they would obtain a macromolecule with polyconjugation. If they went to the right they would also receive such a macromolecule. The first problem is which is the well-trod and easiest path to take? The second and most important problem is which polymer will possess the best electrophysical properties? Up to now we have been speaking of a molecule. But chemists never deal with individual macromolecules. It is impossible to take them in an isolated manner and place them on the operating table of chemical transformation. A polymer participates in the process, and this is not a simple sum of macromolecules but a complex system in which electrical conductivity depends not only on the properties of the macromolecule itself.

In order for current to pass through the polymer its carriers (electrons or "holes") must be able to move freely along the molecules and jump from one to another. This is not an easy matter, for it depends on the distance between molecules, on their quantity per unit of volume and on the presence of chemical bonds between them -- the bridges along which the carriers of the current can travel. It is here at the transition point from molecule to polymer that the greatest difficulties lie.

All of this explains the specific feature of the job; both the complexity of the search -- it often proceeds through the fog of uncertainty -- and the fact that the results, no matter how fine they might seem, are not the final answer. These are rather the first swallows announcing the coming spring in the chemistry of polymer semi-conductors.

What Sort of Spring Will It Be?

It is not necessary to have a fecund imagination in order to draw a picture of the possibilities opening up with the use of polymer semiconductors in the various fields of technology. These prospects are naturally connected not simply with the replacement of crystalline semiconductors by polymers. But even in this case the benefits which might accrue could be quite substantial, since polymer semiconductors are cheaper and simpler to produce. The raw material from which they can be obtained is quite abundant, for this is natural gas and petroleum. But the most important thing is determined by completely new forms of articles, unusual for present semiconductor technology: polymers mean films, fibers, fabrics, pressed powders, etc. If organic semiconductors will be able to preserve the tremendous variety and qualities of ordinary polymers, the range of application of semiconductors will expand to a colossal degree as will the potential of semiconductor technology.

One can imagine entire "sheets" of semiconductor fabric hanging in the sun and transforming its energy into electricity: one can imagine a radio which folds up like a handkerchief into one's jacket pocket. We can dream of elastic tubular chemical reactors, the very walls of which serve as catalysts and still many other seemingly improbable things. But this is not sheer phantasy. These may be suppositions, but projects are being conducted right now which are building the bridge from the present to the future. Begun several years ago by a group of Soviet scientists, these research projects not only have become one of the most promising trends in chemistry, but have won world-wide recognition. In the summer of 1960 an international symposium on macromolecular chemistry was held in Moscow. Afterwards the prominent French chemist, professor at the Sorbonne, Michel Maga (Russian transliteration⁷) stated: "In my opinion one of the most eminent research projects in recent times has been the work of academicians A. V. Topchiyev, V. A. Kargin and their colleagues in imparting the properties of semiconductors to polymers".

At present it is even difficult to foresee how these projects will progress. Each day, each new experiment can bring the unexpected, both pleasant and unpleasant. Naturally we can and must dream: work without thought to the future is a living corpse. But often reality turns out to be greater than the boldest suppositions. This is not due to lack of phantasy (neither scientists nor particularly journalists can be accused of this) but due the riches and the

endless diversity of science. Attitudes can vary toward the prospects of using polymer semiconductors as they can toward the polymers themselves: it is easy to find cause for doubts. Each research project, as everything that is done for the first time, faces difficulties, uncertainties and failures. Those scientists conducting the research understand this as well as anyone else. But every scientific project, and this includes the successful ones, begins from something. Nothing will grow on barren ground. The important thing is that the groundwork has been laid, the groundwork of a great future.